

METHOD FOR THE CATALYTIC PURIFICATION OF LIGHT HYDROCARBONS

5 The present invention relates to a method of purification of light hydrocarbons containing sulfur compounds and/or nitrogen compounds which are refractory to the usual catalytic hydrofining treatments, such as thiophene compounds and compounds
10 of the pyrrole type, by oxidative polymerization of these compounds. It also relates to the regeneration and reactivation of the oxidizing agent used in this method. This method is intended more particularly for
15 the treatment of gasolines, notably gasolines obtained from catalytic cracking, and hydrocarbons obtained from steam cracking of naphthas containing refractory compounds.

By "compounds that are refractory to the usual catalytic hydrofining treatments", we mean thiophene, benzothiophene and their alkylated derivatives, as well as pyrrole and its derivatives, benzopyrrole and carbazole, optionally alkylated.

25 Usually, appreciable amounts of these thiophenic gasolines are added to more-desulfurized gasolines from direct distillation, which are sold in filling station networks, and it is essentially these thiophene compounds contained in the thiophenic gasolines which
30 generate sulfur dioxide in automobile exhausts. The nitrogen-containing compounds present in these products are familiar from their harmful effects on the activity and life of the catalysts used.

35 Furthermore, these refractory compounds are well known in industry owing to the difficulty of removing them. However, it is becoming increasingly necessary to remove these compounds from light hydrocarbons because, notably for the sulfur-containing refractory compounds,

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the environmental restrictions, in Europe as well as in the USA or Japan, and particularly restrictions on sulfur emissions to atmosphere, are becoming more and more stringent. At present, the maximum permitted in 5 gasolines is 150 ppm of total sulfur. However, international agencies are asking for sulfur in gasolines to be limited to less than 50 ppm of total sulfur by 2005 and envisage restriction to less than 10 ppm of total sulfur from 2009 for all products. In 10 thiophenic hydrocarbons, for example gasolines or naphthas, these contents are well above 100 ppm and are generally between 100 and 1000 ppm of total sulfur.

Mixing with desulfurized and denitrogenated gasolines 15 is the only way of disposing of the stocks of gasolines obtained from fluid catalytic cracking (FCC) or of pyrolysis gasolines.

To remove thiophene and its derivatives from thiophenic 20 gasolines, it was proposed, in US patent 6,338,788, to extract the thiophene compounds from the charge by mixing the latter with an electrolyte and a solvent. The resulting mixture is fed into an electrochemical cell, so as to oligomerize the thiophene compounds. The 25 oligomers are removed from the charge subsequently. The electrolyte/solvent mixture can be recovered and recycled in a new mixture with the charge to be treated. The preferred solvents are generally compounds that are able to form complexes with the aromatic 30 compounds present in the hydrocarbons, such as alkylene carbonates, benzonitriles, sulfolanes or derivatives of morpholine. Salts that are used are the tetraalkylammonium salts, such as fluoroborates, fluorophosphates or halides. Apart from the difficulty 35 of implementing this technique with an electrochemical cell on an industrial scale, such a method becomes prohibitive for refiners, when it is necessary to purchase the required solvents and electrolytes, and in addition recycle them for reasons of environmental.

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protection.

Another possible solution is the one disclosed in US patent 4,188,285. There it is proposed to remove the 5 thiophenes from gasolines by bringing gasoline from C₅ to C₇ into contact with a catalyst comprising a zeolite of the faujasite Y type exchanged with silver, at a temperature between 20 and 370°C, and an hourly space 10 velocity between 0.1 and 20. Here, the silver atom is exchanged on the faujasite. In such an operation, the proportion of olefins remains unchanged before and after treatment of the gasoline. In that patent, it is a question of adsorbing the thiophene and its alkylated 15 derivatives on zeolite Y exchanged with Ag⁺ and Cu²⁺ ions utilizing complexing effects using formation of π bonds, the copper being reduced to Cu⁺ as described by Ralph T. Yang et al., in Science & Technology, Vol. 301, p.79, and in Ind.Eng.Chem.Res. 2001, 40, 6236-6239, or by A. Hernandez-Maldonado et al., in Ind.Chem.Res. 20 2003, 42, 3103-3110.

The present applicant has investigated a method of purification of light hydrocarbons containing sulfur-containing and/or nitrogen-containing compounds that 25 are refractory to catalytic hydrofining treatments, which aims to make these compounds heavier by oxidative polymerization of the latter, so that they can be removed more easily from these hydrocarbons. In this 30 method of purification, the applicant aims to achieve not only desulfurization and denitrogenation, but also regeneration of the activity of the oxidizing agent used, by combining the reaction of oxidation with a process of regeneration and activation of the oxidizing agent used.

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The present invention therefore relates to a method of purification of light hydrocarbons with cut point between 20 and 250°C, containing sulfur compounds and/or nitrogen compounds that are refractory to the

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usual hydrofining treatments, characterized in that it comprises

(a) a stage of oxidative polymerization of the compounds comprising an -X-CH= group in a hydrocarbon ring with 5 to 6 ring members, where X represents a sulfur atom or a nitrogen atom, in the presence of at least one oxidizing agent selected from the metal cations,

(b) a stage of separation of the polymers formed and of the oxidizing agent with the light hydrocarbons, and

(c) a stage of oxidation of the metal cation,

these stages being carried out in that order, it being possible for each of these stages to be combined with at least the next stage.

Within the scope of the present invention, the compounds containing an -X-CH= group in a 5-6-membered hydrocarbon ring are thiophene compounds, ranging from thiophene to its alkylated or aralkylated derivatives, and pyrrole compounds, ranging from pyrrole to its alkylated or aralkylated derivatives, generally present in the hydrocarbons and constituting products that are refractory to desulfurization and/or denitrogenation by conventional treatments of catalytic hydrogenation.

To carry out the invention, the metal cations are introduced in liquid form, dispersed or dissolved in an aqueous or organic liquid, or supported on a solid. The method according to the invention is therefore a multiphase process with two or three phases, depending on whether or not the metal cations are deposited on a solid support before the start of the reaction employed in this method, namely a polymerization of the sulfur compounds and/or nitrogen compounds.

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Within the scope of the present invention, when the metal cations are immobilized on a solid support in the fixed or moving bed, the polymerization reaction takes place starting at room temperature, under atmospheric pressure, at an hourly space velocity (HSV) of at least 5 0.1 h^{-1} .

In general, for the metal cations to polymerize the sulfur compounds and/or nitrogen compounds, the 10 oxidizing metal cation must have a redox potential greater than that of the molecule to be oxidized/polymerized in the reaction mixture.

To achieve redox potentials such as permit the 15 polymerization of the thiophene or pyrrole compounds, the metal cation is selected from the cations of metallic elements of the group comprising iron, copper, molybdenum, cerium, manganese and vanadium, and each of these metals must be present in the reaction mixture 20 with a degree of oxidation of at least 2. These metal cations are used in the form of salts of the group comprising the halides, nitrates, citrates, carboxylates, phosphates, sulfates, persulfates, borates, perborates and the bidentate and polydentate 25 complexes of linear or cyclic form, containing atoms of nitrogen, sulfur and/or oxygen as the coordinating element. By bidentate and polydentate complexes we mean, non-limitatively, the phthalocyanines, porphyrins, cyclamines, bipyridines and Saler complexes.

30 When the metal cation is introduced in the dispersed state or in solution in water, the polymerization reaction is a liquid/liquid (organic/aqueous) two-phase reaction, and the polymers formed and the oxidizing 35 cations can be removed by the decanting of separated phases, by filtration and/or extraction by techniques that are well known to a person skilled in the art.

In another embodiment of the invention, the method is

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carried out in the presence of a solid selected from the group comprising charcoal, clays, zeolites, molecular sieves, amorphous aluminosilicates, alkaline silicates, silicoborates, silica-magnesias, and 5 aluminophosphates. This solid can support the salts of the metal cations required for the invention, whether or not there is ionic interaction between these cations and these solids.

10 In a preferred embodiment, the protons initially present on the support were exchanged for metal cations, then these metal cations were oxidized before use, making it possible to obtain an oxidation state of these metals greater than or equal to two. This 15 oxidation state is essential for the polymerization reaction to take place in the hydrocarbons, as had already been found by Bein for media that are less complex than the hydrocarbons obtained from petroleum distillation, in his article in Studies in Surface 20 Science and Catalysis, Vol. 102, 1996, pp. 295-319.

The advantage of a method employing the metal cation in the form of counter-ion of a solid support is that it is possible for the reaction of polymerization to be 25 carried out in the usual conditions of refining, i.e. with a catalyst bed of the types used in refining. Another advantage is that it is possible to envisage in-situ or ex-situ regeneration of the metal cations used as oxidizing agent.

30 The following may be chosen as support of the metal cations: crystalline or amorphous solids, cation exchangers, containing at least one metal from the group of elements comprising silicon, aluminum, 35 zirconium, titanium, germanium, gallium and boron, used alone or in combination, and with specific surface of at least 10 cm²/g.

Preferably, these supports are selected from the clays,

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including the bentonites, and the zeolites, including Sapo, Alpo and Beta, and mesoporous, for example of the type MCM 41, molecular sieves, amorphous aluminosilicates, alkaline silicates, silicoborates, 5 silica-magnesias, these solids having a pore size between 1.5 nm and 200 nm.

To obtain these supported cations, it is necessary to bring the solid into contact with metal cation salts in 10 the form of an aqueous or organic solution, the salts being selected from the nitrates, carboxylates, sulfates, persulfates, citrates, phosphates, borates, perborates and halides of metals, including iron, copper, molybdenum, manganese, vanadium and cerium. The 15 preferred salts are selected from ferric chloride, cuprous chloride, molybdenum chloride, vanadium oxychloride and cerium chloride.

Preferably, the amount of metal cation present on the 20 support can vary from 0.1 wt.% to 30 wt.% of the metal corresponding to said cation.

These supported cations can exert their action in a fixed-bed, moving-bed or fluidized-bed process or in 25 suspension in a liquid.

In the course of polymerization of the sulfur compounds and/or nitrogen compounds, the polymers formed are entrained in suspension in the hydrocarbon or deposited 30 on the solid. They can therefore be extracted, decanted, filtered or even distilled, in order to be removed from the hydrocarbon thus purified. When the polymers formed are deposited on the solid, the removal stage comprises extracting the polymers deposited on 35 the support by washing with solvent, notably by charging, by desorption by a stream of inert gas selected from helium, nitrogen, carbon dioxide and water vapour, at a temperature above 100°C, and/or by combustion by injecting air or oxygen, preferably after

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removal of the light hydrocarbons still present on the particles of support.

5 To restore or maintain the supported cation in an oxidation state sufficient for the reaction of polymerization to take place normally, the metal cation is oxidized. This stage of oxidation of the metal cation, whether or not it is supported, comprises restoring the metal cations to a degree of oxidation of 10 at least 2, by oxidation, by injecting air or liquids containing peroxides or other metal cations that are more oxidizing, optionally simultaneously increasing the temperature of the oxidizing agent.

15 In a preferred embodiment of the invention, it is possible for the stages used alone or in combination to be combined in a continuous process or a batch process. Thus, at the end of the stage of oxidation of the metals, the oxidized metal cation is reused directly 20 for a new stage of oxidative polymerization. Moreover, carrying out certain stages of the method, for example the first stage of oxidative polymerization and the second stage of removal of the polymers obtained, which are present in the liquid phase and/or on the support, 25 when a support is used, would remain within the scope of the invention. The same would apply if we combine the stage of removal of the polymers obtained and the third stage of oxidation of the metal cation. An embodiment of the method simultaneously combining the 30 third and the first stage, or even the three stages depending on the type of fixed or moving bed that can be employed, also falls within the scope of the present invention.

35 Another object of the invention is the application of this method to the finishing treatment of industrial streams containing refractory sulfur-containing or nitrogen-containing compounds. More particularly, this method can be used for the desulfurization/

denitrogenation of gasolines produced by catalytic cracking and of effluents from the steam cracking plant, notably pyrolysis gasolines. This method can also be applied as finishing treatment for aromatic effluents such as benzene, toluene and xylene.

The following example is given for the purpose of illustrating the invention, though without wishing to limit its scope.

10

Example

The present example describes several embodiments of the method of the invention, using various oxidizing cations, and their efficiency with respect to 15 desulfurization and/or denitrogenation.

TEST I:

FeCl₃ powder is suspended in a gasoline from catalytic cracking or LCCS by mixing at a temperature of 25°C. The Fe/S ratio (total sulfur in the LCCS) is 16 atoms of Fe per atom of sulfur (16 atoms/atom).

TEST II:

25 Anhydrous FeCl_3 is deposited on silica: the supported cation thus formed is mixed with LCCS at 40°C. The Fe/S ratio is 13 atoms/atom.

TEST III:

30 Anhydrous FeCl_3 is deposited on activated charcoal: the supported cation thus formed is mixed with LCCS at 40°C. The Fe/S ratio is 13 atoms/atom.

TEST IV:

A zeolite β is charged with sodium, in the form of particles from 0.15 to 0.5 mm, exchanged with copper acetate, in a tubular reactor, and LCCS is circulated through it at an hourly space velocity of 1.2 h^{-1} and at a temperature of about 25°C , at atmospheric pressure. The effluent is analyzed for sulfur and/or nitrogen

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after circulation for 3 hours and after 15 hours.

TEST V:

A zeolite β is charged with sodium in the form of particles from 0.15 to 0.5 mm, exchanged with copper acetate, in a tubular reactor, and LCCS is circulated through it at an hourly space velocity of 1.2 h^{-1} and at a temperature of about 150°C , at atmospheric pressure. The effluent is analyzed for sulfur and/or nitrogen after circulation for 1 h 30 min and after 14 hours.

TEST VI:

Test V is repeated four times, with each test lasting 7 hours. The supported cation is reactivated in accordance with stages 2 and 3 described above, these stages being simultaneous and carried out with circulation of air, for 5 hours, at 350°C .

The zeolite β is charged with sodium exchanged with copper II thus reactivated in a tubular reactor and LCCS is again circulated through it at an hourly space velocity of 1.2 h^{-1} and at a temperature of about 150°C , at atmospheric pressure. The effluent is analyzed for sulfur and/or nitrogen after circulation for 1 h 30 min and after 3.5 hours.

TEST VII:

A zeolite β initially in protonated form, with particle size varying from 0.15 to 0.5 mm, is exchanged with copper acetate, and is then mixed with LCCS at a temperature of about 40°C , at atmospheric pressure. The Cu/S ratio is 0.96 atom/atom. The effluent is analyzed for sulfur and/or nitrogen after 7 hours.

TEST VIII:

A zeolite β with sodium in the form of particles from 0.15 to 0.5 mm, exchanged with copper acetate, is mixed with LCCS at 40°C . The Cu/S ratio is 10.3 atoms/atom. The effluent is analyzed for sulfur and/or nitrogen

after 6 hours.

TEST IX:

5 A zeolite β with sodium in the form of particles from 0.15 to 0.5 mm, exchanged with copper acetate, is mixed with LCCS at 40°C. The Cu/S ratio is 30.8 atoms/atom. The effluent is analyzed for sulfur and/or nitrogen after 5 hours 30 minutes.

10 TEST X:

A zeolite β with sodium, in the form of particles from 0.15 to 0.5 mm, exchanged with copper acetate, is mixed at 40°C with a model fluid containing 0.5 wt.% thiophene, 0.5 wt.% dodecane and 99 wt.% toluene. The 15 Cu/S ratio is 1.5 atom/atom. The effluent is analyzed for thiophene and mercaptans after 6 hours 30 minutes.

TEST XI:

An emulsion is prepared at room temperature from 202 g 20 of organic solution containing 99 wt.% toluene, 0.5 wt.% pyrrole and 0.5 wt.% n-decane, with 112 g of aqueous solution of FeCl_3 at 6.4 wt.%. The Fe/N ratio is 2.94 atoms/atom. Analyses for total nitrogen are carried out after 5 hours.

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TEST XII:

An emulsion is prepared at room temperature from 200 g of organic solution containing 99 wt.% toluene, 0.5 wt.% pyrrole and 0.5 wt.% n-decane, with an aqueous 30 solution of $\text{Ce}(\text{SO}_4)_2$ at 30 wt.%. The Ce/N ratio is 4.7 atoms/atom. Analyses for total nitrogen are carried out after 40 minutes.

TEST XIII:

35 4.3 g of anhydrous powder of FeCl_3 is dispersed in 183 g of a solution containing 99.25 wt.% toluene, 0.5 wt.% thiophene and 0.25 wt.% dodecane, at 30°C. The Fe/S ratio is 2.45 atoms/atom. Analyses for total sulfur are carried out after 2 hours.

TEST XIV:

A zeolite β in powder form, initially in protonated form, is exchanged with copper acetate, and is then 5 mixed with 200 g of a solution containing 99.25 wt.% toluene, 0.5 wt.% thiophene and 0.25 wt.% dodecane, at a temperature of about 40°C and at atmospheric pressure. The Cu/S ratio is 0.8 atom/atom. Analyses for total sulfur are carried out after 4 hours.

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The results obtained in desulfurization and denitrogenation are given in the following table, in which the contents of sulfur and of nitrogen are expressed in ppm.

15

Table

Test	S(total)		S(thiophene)		S(2+3methylthiophene)		N(total)	
	(inlet)	(outlet)	(inlet)	(outlet)	(inlet)	(outlet)	(inlet)	(outlet)
I	121	94	60	54	50	35	-	-
II	121	80	60	49	50	35	-	-
III	121	97	60	46	50	46	-	-
IV	113	70	53	28	50	36	-	-
	113	93	53	44	50	36	-	-
V	121	31	57	23	53	6	-	-
	121	76	57	35	53	37	-	-
VI	105	46	-	-	-	-	-	-
	105	70	-	-	-	-	17	1.7
VII	215	166	39	26	122	117	-	-
VIII	121	84	60	40	50	36	-	-
IX	121	93	57	36	53	49	-	-
X	-	-	2074	1064	-	-	-	-
XI	-	-	-	-	-	-	1050	597
XII	-	-	-	-	-	-	1050	177
XIII	-	-	1900	733	-	-	-	-
XIV	-	-	1900	488	-	-	-	-

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